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Trial Measurements Aboard a Moored Submarine

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Naval Medical Research and Development Command
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W. C. Milroy, CAPT MC USN
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SUMMARY PAGE

PROBLEM. The Naval Medical Research and Development Command was asked to initiate biomedical research aimed toward improving the submarine atmosphere control program. **The proposed objective was to assemble a list of atmospheric contaminants according to priority for (potential) toxicological effects.**

FINDINGS. Expired breath samples were collected from crewmembers in the forward space, torpedo room, forward engine space, and engineering space of a fast-attack submarine. Analysis by computer-assisted, gas chromatography/mass spectrometry (GC/MS/COMP) provided chromatograms indicating similar volatile organic compounds (VOC's) between samples. Each chromatogram contained an average of 468 VOC's. Computer analysis characterized 192 of the VOC's collected in the torpedo room. The total concentration of VOC's, > 881 ppb, contained 348 ppb of C_7-C_{11} acyclic alkanes. With the possible exception of benzene, none of the VOC's exceeded the 90-day limits of exposure in nuclear submarines. In this trial study, the method of sample collection did not permit discrimination between VOC's desorbed from the body and atmospheric VOC's present in the airways.

APPLICATION. The GC/MS/COMP technique is adaptable for use in estimating the body burden of VOC's aboard submarines. **Estimations of body burdens will provide the Navy with an additional guideline for prioritizing gaseous contaminants and judging the quality of air in submarine atmospheres.** Selective use of the GC/MS/COMP technique may also prove useful for evaluating operational problems, such as the minimum required frequency of snorkeling.

Administrative Information

This investigation was conducted under research work unit MR0001 001-5093. It was submitted for review on 12 December 1984 and approved for publication as Memorandum Report 84-4 on 19 December 1984.

ABSTRACT

The success of the submarine atmosphere control program has depended solely upon periodic identification of contaminants in the ship's atmosphere. Substances found to exceed safeguard concentrations are controlled by restricting their use aboard ship or scrubbing them from the atmosphere. But, this approach tends to ignore the human host. Advancements in technology now enable biomedical scientists to identify organic gases absorbed by the human body during exposures to industrial environments. We evaluated the potential application of computer-assisted, gas chromatography/mass spectrometry (GC/MS/COMP) to the measurement of volatile organic compounds (VOC's) absorbed by submarine crewmembers. Expired breath samples were collected from watchstanders stationed in the forward space, torpedo room, forward engine space, and engineering space of a fast-attack submarine. Analysis of the samples showed a remarkably complex mixture of VOC's with an average of 408 compounds per sample. Without benzene, the total concentration of organic vapors, 3 mg/m^3, was well below the maximum allowable concentration of total hydrocarbons (70 mg/m^3) for 90 continuous days aboard submarines. Benzene overloaded the sample collector and therefore existed in a concentration > 80 ppb. Since all crewmembers were smokers, one possible source of benzene was residual organic vapors in the lung. Thirteen of the 17 highest concentrations of VOC's were acyclic, C_7-C_{11} alkanes. Assuming that most of the expired VOC's were derived from the submarine, the hydrocarbon composition of the atmosphere was more concentrated and complex than in residential dwellings. This indicates that crewmembers absorb atmospheric VOC's during patrol and desorb the contaminants at home. Future work should attempt to; (a.) measure desorption of VOC's from the body after patrol, and (b.) evaluate the VOC's likely to overload the sample collector during 20-liter collections of the submarine atmosphere. The desorption of trace contaminants from the body will indicate a body burden of organic substances. > Estimations of body burdens can provide the Navy with an additional guideline for prioritizing gaseous contaminants and judging the quality of air in submarine atmospheres. < Selective use of the GC/MS/COMP technique may also prove useful for evaluating operational problems, such as the minimum required frequency of snorkeling.

TERMINOLOGY AND ABBREVIATIONS

B_s. The body burden of organic substance. The amount of organic vapor absorbed by the body.

$C_{s,e,min}$. The minimal concentration of an organic substance in the expired breath.

GC/MS/COMP. Computer-assisted, gas chromatograpny and mass spectrometry.

$F_{s,max}$. The maximal concentration of an organic vapor in the atmosphere.

GC. Gas chromatography.

MS. Mass spectrometry.

P_s. The potential for accumulating an organic substance in the body by pulmonary ventiltion.

{R} trademark.

S_e. The quantity of organic vapor expired from the body.

subscript s. An organic substance in its gas phase.

subscript e. Expired.

subscript min. Minimum.

subscript max. Maximum.

THC. Total hydrocarbons concentration.

V_e. The volume of expired gas.

VOC. Volatile organic compound.

INTRODUCTION

The Chief of Naval Operations (8) asked the Naval Medical Research and Development Command to institute research aimed toward improving the atmosphere control program aboard nuclear submarines. Three research efforts were specified:

- Identify the contaminants in nuclear submarines, using methodology developed by the Naval Research Laboratory.
- List the contaminants by priority.
- Perform toxicology studies in animals on high priority contaminants.

ORGANIC VAPORS IN NUCLEAR SUBMARINES. It has been known for years that a variety of hydrocarbons exist in submarine atmospheres, but results of previous assays may no longer represent the quantity and quality of atmosphere contaminants in new classes of submarines. Analysis of the composition of total hydrocarbon's is not simple and straightforward, since more than 12,000 organic contaminants may exist in submarines as a consequence of smoking (13). The atmospheres of the Navy's first nuclear submarines were composed of aliphatic paraffins, cycloparaffins, olefins, and aromatic contaminants (table 1). The major source of contaminants was oil-based paints which were periodiclly applied to the inboard surfaces during refitting of the ships. Consequently, total hydrocarbon concentrations were higher before submersion (89-105 mg/m^3) than during the first 122 hours of submersion (30-90 mg/m^3) (10). In addition to these sources, non-aromatic hydrocarbons originated from humans (eg methane), oils, cooking products, and the decomposition of hot oil (1).

The aromatic hydrocarbons constituted about 50% of the hydrocarbons in 1958-1959 and 25-30% of the total hydrocarbon content in 1960-1963. It did not take long for aromatic hydrocarbons to accumulate in the atmosphere, since their content was nearly the same whether sampling was done early or late in the cruise. Xylene and trimethylbenzene constituted approximately 50% of the mixture of aromatic hydrocarbons recovered from submarine air. Major sources of aromatic hydrocarbons were lighter fluids, cements, and tobacco smoke. Likely sources of aromatic hydrocarbons were paint solvents, mineral spirits, and diesel

Table 1. Trends in Levels of Organic Vapors Aboard Nuclear Submarines.

Ref.	Yr.	Site(s)	Collector	Assay	Results
10	1956-1958	Main air filters	Activated charcoal	Infrared and mass spectrometers	THC = 50-171 mg/m^3
10	1959	Varied	Activated charcoal		THC = 47-52 mg/m^3
16	1959	---	Chromosorb	GC, with argon ionization detection	THC = 110-186 mg/m^3.
1	1960	---	---	---	THC = 100 mg/m^3 Aromatics = 2.98 ppm Olefins and alicyclics $\leq$ 12.5 mg/m^3
4	1961	---	Activated charcoal	GC, with fluorescent indicator absorption.	THC = 133 mg/m^3 Aromatics = 33.5 mg/m^3
1	1970	---	---	---	THC = 30 mg/m^3 Aromatics = 0.85 ppm Olefins and alicyclics $\leq$ 4 mg/m^3
1	1978	---	---	---	THC = 10 mg/m^3 Aromatics < 0.9 ppm Olefins and alicyclics $\leq$ 1 mg/m^3
12	1983	---	---	---	THC < 60 mg/m^3

[The prevalent use of activated charcoal as a collecting agent led to a 2-fold underestimation of the total hydrocarbons because low molecular weight hydrocarbons passed through the carbon bed (16).

Reference 1 included the following compounds in the aromatics and olefin-alicyclics:

AROMATICS. Benzene, Toluene, Xylene, Ethylbenzene, Propylbenzene, Mesitylene, Ethyltoluene, Pseudocumene, and Indane.

OLEFIN-ALICYCLICS. Acetylene, Ethylene, Propylene, Butene, Isoprene, Decene, Methylcyclohexane, Ethylcyclohexane.]

fuel vapors (4).

Improvements of the atmosphere control program in the decades of the 1960's and 1970's caused the levels of total hydrocarbons to drop by 1 order of magnitude. Potentially toxic substances were prohibited aboard ship and the practice of painting was sharply curtailed. The requirements for maintenance of the engineering plant were upgraded and engineering capabilities for revitalizing the air were improved (1).

Today, organic vapors are "scrubbed" from the submarine atmosphere by absorption and catalytic oxidation. Activated charcoal is effective in absorbing aromatic hydrocarbons, C_6-C_n aliphatic hydrocarbons, chlorinated hydrocarbons (except dichloroacetylene), and freons. Hydrocarbons can return to the atmosphere when the carbon becomes saturated. Freons are eventually desorbed when displaced by heavier, higher boiling hydrocarbons. A large decrease in partial pressure of contaminant gases, such as occurs when shifting from high to low barometric pressure, will also desorb hydrocarbons from activated charcoal.

Hopcalite {R} catalyzes the oxidation of hydrocarbons when heated to 600^{o}F inside the catalytic burner. The catalytic burner removes aromatic hydrocarbons, C_6-C_n aliphatic hydrocarbons, ketones, aldehydes, ethers, and monoethanolamines. Halogenated hydrocarbons are decomposed to hydrochloric acid, hydrofluoric acid, and vinylidene chloride, before removal by lithium carbonate downstream of the catalytic burner. Dichloroacetylene, which may form in a heated alkali scrubber, is extremely toxic (1).

Sea trials of the trident class submarine have indicated a remarkable reduction of atmospheric hydrocarbon levels since the first nuclear submarines went to sea. Recent measurements showed the total hydrocarbon concentration to rise from 31 ppm to 49 ppm in the engine room between the 2nd and 4th days of closed-boat operation. The composition of total organic substances was estimated to be 80-95% aliphatic hydrocarbons. GC/MS analyses of all samples indicated no concentrations of trace contaminants in excess of 1 ppm. No localized concentrations of hydrocarbons were detected, but hydrocarbon concentrations increased from forward to aft with an abrupt increase occurring upon entering the engine room. This was explained by a high number of hydrocarbon sources in the engine room relative to location of the charcoal bed in the forward compartment's main fan room (12).

The potential for accumulating any organic substance by pulmonary ventilation (F_s) should be proportional to the gradient between maximal concentration in ambient air ($F_{s,max}$) and minimal concentration expired ($C_{s,e,min}$). At present, there is little data on when and where $F_{s,max}$

$$\text{eq. 1} \qquad F_s \propto (F_{s,max} - C_{s,e,min})$$

occurs aboard submarines. $C_{s,e}$ will change with bioaccumulation of "s", contamination of the body by non-pulmonary mechanisms, and vascular transport of metabolic products to the lung.

Various classes of hydrocarbon contaminants have compounds which are particularly toxic agents (table 2). Since these toxic agents may be

Table 2. Toxic Organic Vapors

Ref.	Class	Compound	Toxic Effect
1	Aromatic hydrocarbons	Benzene	Tumors of blood forming tissues.
		Xylene	Impairment of coordination and reaction time.
		Toluene	Impairment of coordination and reaction time.
1	Chlorinated hydrocarbons	Methylchloroform	Narcosis.
		Trichloroethylene	Cardiac failure and liver damage.
		Methylene chloride	Strong irritant.
		Tetrachloroethylene	Strong irritant.

present in very low concentrations, emphasis has been placed on quantifying the toxicity of the entire mixture of organic vapors. The current practice is to assume that the toxic effects of all substances are additive (1,11). To quantify the toxicity, the concentration of every substance is divided by its maximum allowable concentration. The sum of the quotients indicates a toxic mixture when it exceeds a value of 1. Use of this method indicated that the total organic vapors exceeded their toxic limits during the 1960's, with values of 1-1.12 for the sum of the quotients. By 1979, the sum of the quotients dropped to 0.52 (1).

BODY BURDEN. Since organic vapors must be absorbed by the human body before they can exert a toxic effect, it would be adventageous to quantify the body burden of organic vapors from exposure to submarines. The absorption of organic vapors during a submarine patrol is analogous to inhaling an anesthetic gas prior to surgery. In either situation, desorption begins when the body ventilates with clean air. Therefore, the amount of organic substance absorbed by the body (B_s) through the lung can be estimated by measuring the quantity of substance expired (S_e) right after cessation of occupational exposure. S_e depends on the

eq. 2 $$S_e \propto B_s$$

eq. 3 $$S_e = C_{s,e} * V_e$$

rate of ventilation, tissue solubility of "s", metabolic rate, and time lapse following exposure.

The change of S_e with time is depicted by a graphic plot of $C_{s,e}$ (log ordinate) as a function of elapsed time after exposure (abscissa). The plot, called a breath decay curve, can be used to estimate the magnitude of bioaccumulation by comparing post-exposure decay of S_e to control decay of S_e (15).

If samples can be collected aboard submarines, the GC/MS/COMP technique may be very useful for measuring trace VOC's in human expired breath and the submarine atmosphere (14). The GC/MS/COMP technique is frequently used to characterize and quantify complex mixtures of VOC's, since it is capable of identifying individual organic components in amounts as little as 1-10 ng (2,11,14,17). GC/MS is sufficiently sensitive to measure hydrocarbons in concentrations of parts per trillion (14).

METHODS

DESIGN. Trial measurements were performed aboard a submarine moored at the New London Submarine Base. The original plan was to perform simultaneous measurements of expired- and atmospheric hydrocarbons as the first step toward documenting organic contaminants being absorbed by the tissues of the body (APPENDIX). Sudden deployment of the submarine cancelled the study only hours after the investigative team assembled in Groton. Since the team could not remain assembled indefinitely, it was necessary to obtain expired breath samples under unmonitored conditions.

PROTOCOL. Four teflon bags were flushed with ultrapure air and capped for transfer aboard ship. The Executive Officer, USS Gato, handed a teflon bag to each watchstander (table 3) with instructions to "blow up" the bag with exhaled breath, expel the sample by rolling the bag to the mouthpiece, then reinflate the bag. The third inflation was preserved by capping the mouthpiece. The inflated bags were handed to the investigators who were waiting on the pier adjacent to the moored submarine. The ship had been ventilating with surface air for at least 24 hours while being occupied by 1/3[rd] of the crew.

table 3: Subjects

Subject	Age	Naval Rating
A	20	machinist's mate
B	33	electronic's technician
C	23	machinist's mate
D	30	torpedoman

[All men were smokers. Except for subject A, all men were qualified in submarines.]

In the laboratory, a constant flow pump (300 ml/min) suctioned each breath sample through a Tenax GC {R} cartridge. The Tenax GC {R} cartridge was sealed in a culture tube and shipped to the associate investigator's laboratory in Chicago. Two additional Tenax GC {R} cartridges were used as blanks.

MEASUREMENT TECHNIQUE. Performance of the assay required sample collection, extraction, and analysis (2,6,13,14,17). During sample collection, volatile organic substances (VOC's) were adsorbed by the

Tenax GC {R} (2,6-diphenyl-p-phenylene oxide polymer) as the gas sample flowed through the sorbent's container.

Adsorbed VOC's were extracted from Tenax GC {R} by the thermal desorption technique. The Tenax GC {R} cartridge was backflushed with helium in order to transfer the VOC's into a nickel capillary trap. The VOC's were condensed by cooling the trap with liquid nitrogen. In those instances where large volumes of water vapor are collected, the samples are subjected to a second transfer step prior to GC/MS/COMP annalysis.

Sample analysis began when the condensate was rapidly heated for vaporization into a carrier gas, helium. The sample was injected into a high-resolution, fused-silica capillary gas chromatography column, for separation of the mixture into component VOC's (14). Effluent from the gas chromatograph entered a mass spectrometer for characterization by electron impact ionization. A computer printed a reconstructed ion chromatogram, which was a rectangular plot of the intensity of extracted ion current (Y axis) against the scan number/sample retention time (X axis) (2,5,17). Each mass spectrum was analyzed by a computer program which identified VOC's by probability of their fit to spectral characteristics of an extensive list of standard compounds.

RESULTS

All samples provided reconstructed ion chromatograms which were remarkably similar between subjects. The total number of VOC's observed in the samples was exceptionally large; namely 486 (sample A), 492 (sample B), 457 (sample C), and 436 (sample D, shown in figures 1,2). The compounds in sample D were characterized by computer analysis if their concentrations exceeded 150,000 counts per component (table 4). The computer identified 152 VOC's with a total concentration of > 861 ppb (ca. 3 mg/m^3, without benzene). Benzene appeared to overload the GC column in each sample, since; (a.) there was a broad peak at spectrum scan number 525 in each sample, and (b.) the concentration of benzene exceeded 80 ppb in sample D. Therefore, the total concentration of acyclic, C_7-C_{11} alkanes (348 ppb) constituted < 40% of all VOC's (table 5). The 17 VOC's present in highest concentrations collectively exceeded 464 ppb (table 6). Thirteen were acyclic hydrocarbons with 6-12 carbon

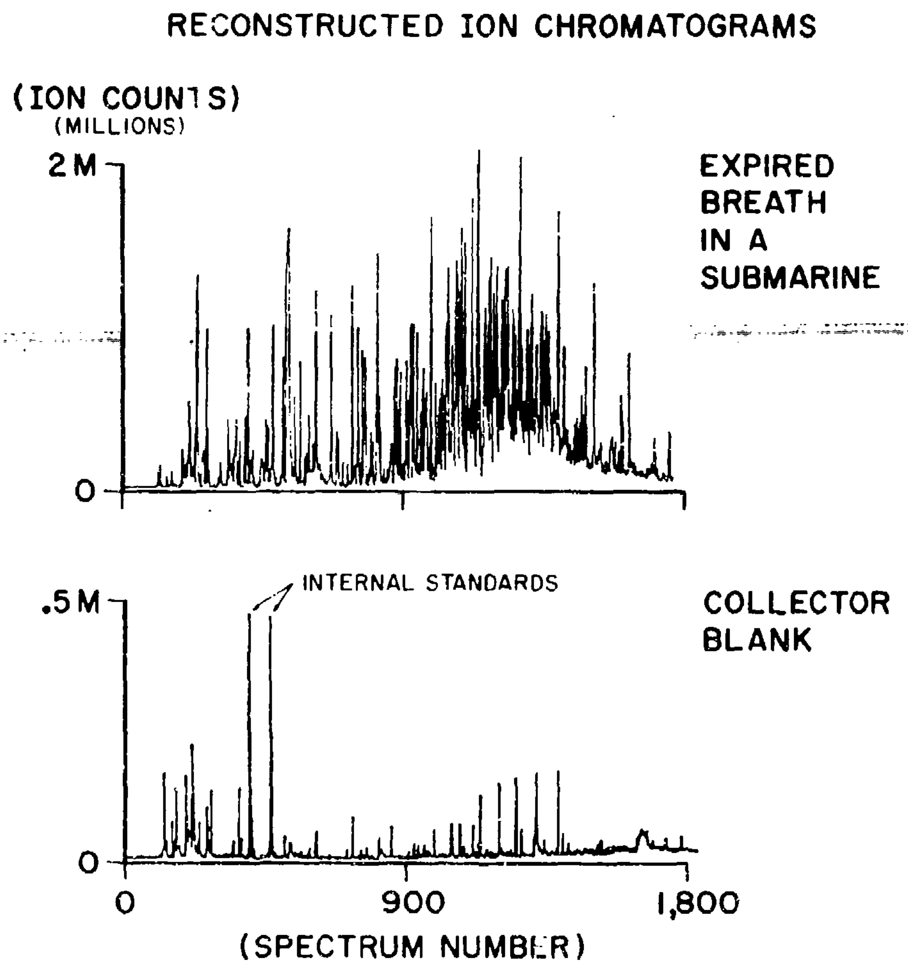

Figure 1: The top panel shows a collection of subject D's expired breath in the torpedo room of the USS Cato. The bottom panel is a collector blank which has been spiked with perfluorobenzene and perfluorotoluene. The peak ion counts for the spiked compounds each represented a concentration of 3 ppb.

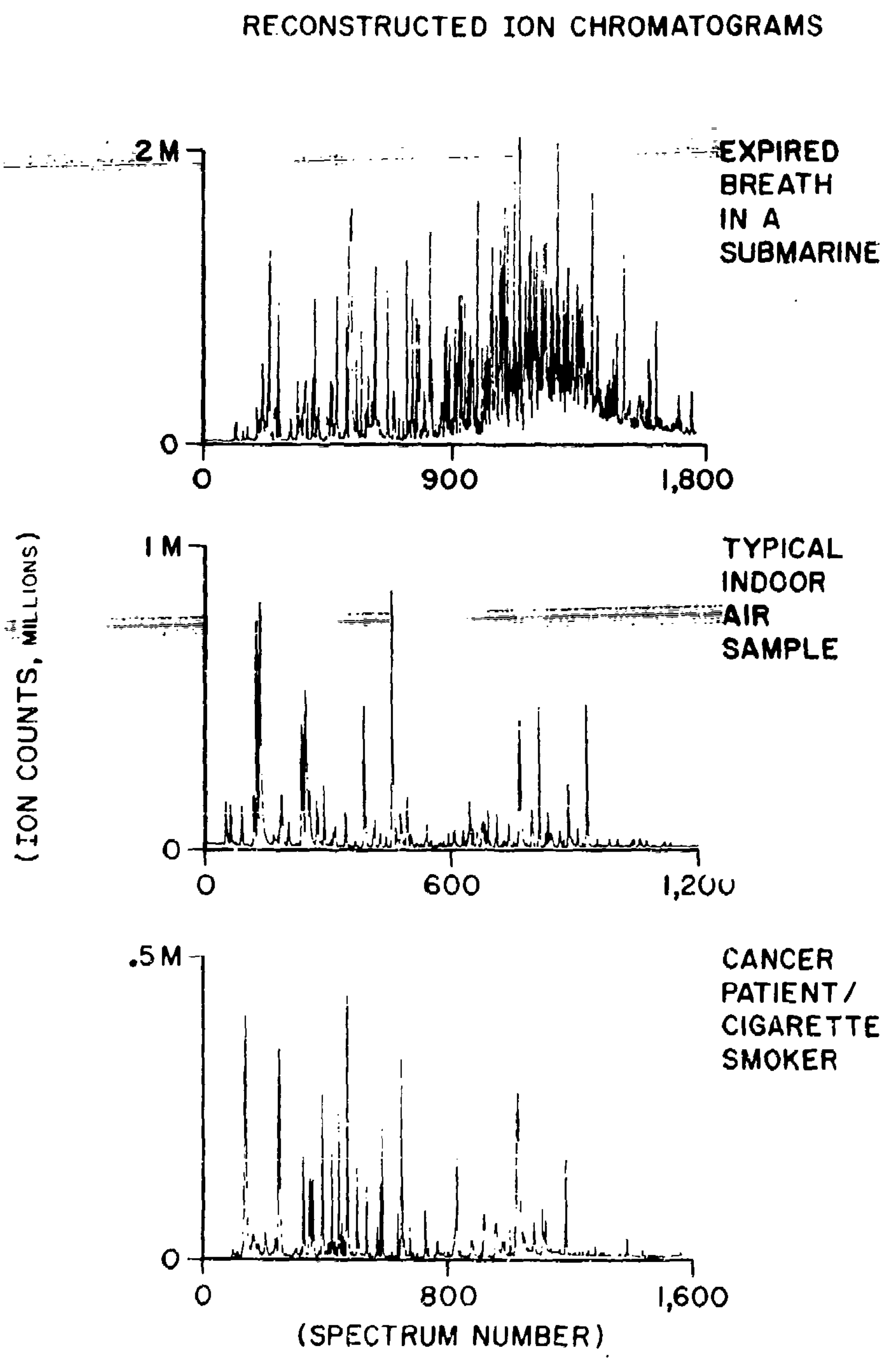

Figure 2: The top panel shows a collection of subject D's expired breath in the torpedo room of the USS Cato. The middle panel characterizes the expired breath of a patient who breathed ultrapure air for 20 minutes before the collection. The bottom panel was collected from a residential building in Chicago. All samples were collected in 20 liter bags and can therefore be used for comparing estimated concentrations by using the magnitudes of ion counts.

TABLE 4. VOLATILE ORGANIC COMPONENTS IDENTIFIED IN BREATH SAMPLE FROM SAILOR ON BOARD USS GATO [SAMPLE FILE SUEA04.DAT]

Spec No.	MW	Formula	Identification	Relative Peak Area ($x10^4$)
202	46	C_2H_6O	Ethanol	21
221	58	C_3H_6O	Acetone	44
234	68	$C_3H_4N_2$	Pyrazole	3
236	60	C_3H_8O	2 propanol	7
239	72	C_5H_{12}	n pentane	20
247	68	C_5H_8	2 methyl butadiene	254
257	96	$C_2H_2Cl_2$	Vinylidene chloride	3
266	70	C_5H_{10}	Methyl butene	9
268	84	CH_2Cl_2	Methylene chloride	17
270	68	C_5H_8	Pentadiene	8
279	186	$C_2Cl_3F_3$	Trifluorotrichloroethane	55
285	66	C_5H_6	Cyclopentadiene	7
323	70	C_4H_6O	3 butynol	12
347	86	C_6H_{14}	Methyl pentane	28
361	72	C_4H_8O	Butanal	12
371	72	C_4H_8O	Methyl ethyl ketone	27
375	88	$C_5H_{12}O$	Methyl butanol	18
388	84	C_6H_{12}	1 hexene	24
402	82	C_5H_6O	2 methyl furan	10
411	86	C_6H_{14}	Hexane	148
419	168	$C_2HCl_3F_2$	Trichlorodifluoroethane	2
421	82	C_5H_6O	Methyl furan	10
426	84	C_6H_{12}	C_6 alkene isomer	13
470	84	C_6H_{12}	Methyl cyclopentane	30
483	82	C_6H_{10}	Hexadiene	42
490	132	$C_2H_3Cl_3$	Trichloroethane	129
496	79	C_5H_5N	Pyridine	4
506	82	C_6H_{10}	Methyl pentadiene	3
525	78	C_6H_6	Benzene	$>$ 80
535	117	CCl_4	Carbon tetrachloride	3
541-2			Supersaturated--unidentified	

TABLE 4. VOLATILE ORGANIC COMPONENTS IDENTIFIED IN BREATH SAMPLE FROM SAILOR ON BOARD USS GATO [SAMPLE FILE SUEA04.DAT] (continued)

Spec No.	MW	Formula	Identification	Relative Peak Area (x10^4)
562	100	C_7H_{16}	2 Methyl hexane	41
581	100	C_7H_{16}	C_7 Alkane	58
596	98	C_7H_{14}	Dimethyl cyclopentane	13
606	130	C_2HCl_3	Trichloroethylene	2
620	88	$C_5H_{12}O$	2 pentanol	11
625	96	C_6H_8O	Dimethyl furan	4
632	100	C_7H_{16}	n heptane	131
633	90	$C_4H_{10}S$	Thiapentane	8
646	74	$C_3H_6O_2$	Propionic acid	7
652	126	C_9H_{18}	Isobutyl cyclopentane	3
656	94	C_6H_6O	Phenol	8
659	98	C_7H_{14}	Heptene	1
677	98	C_7H_{14}	Cycloalkane	88
680	100	$C_6H_{12}O$	Methyl isobutyl ketone	15
700	98	C_7H_{14}	2 n-hexadecylindane	22
717	112	C_8H_{16}	Trimethyl cyclopentane	8
747	92	C_7H_8	Toluene	160
767	114	C_8H_{18}	Dimethyl hexane	204
768	94	C_7H_{10}	Dimethyl cyclopentadiene	65
782	114	C_8H_{18}	3 Methyl heptane	80
790	112	C_8H_{16}	Dimethyl cyclohexane	61
794	112	C_8H_{16}	Octene	16
810	112	C_8H_{16}	Trimethyl cyclopentane	18
816	112	C_8H_{16}	Methyl ethyl cyclopentane	24
828	112	C_8H_{16}	Dimethyl cyclohexane	21
831	114	C_8H_{18}	n octane	195
836	166	C_2Cl_4	Tetrachloroethylene	31
841	112	C_8H_{16}	Dimethyl cyclohexane	14
876	128	$C_8H_{16}O$	Octanone	12
887	128	C_9H_{20}	Dimethyl heptane	43
894	112	C_8H_{16}	Dimethyl hexene	61

TABLE 4. VOLATILE ORGANIC COMPONENTS IDENTIFIED IN BREATH SAMPLE FROM SAILOR ON BOARD USS GATO [SAMPLE FILE SUEA04.DAT] (continued)

Spec No.	MW	Formula	Identification	Relative Peak Area ($x10^4$)
899	128	C_9H_{20}	Tetramethyl pentane	41
904	126	C_9H_{18}	Tetramethyl cyclopentane	37
910	126	C_9H_{18}	Trimethyl cyclohexane	10
913	126	C_9H_{18}	Methyl ethyl cyclohexane	9
924	106	C_8H_{10}	Ethyl benzene	38
929	126	C_9H_{18}	Trimethyl cyclohexane	37
935	128	C_9H_{20}	Dimethyl heptane	58
939	106	C_8H_{10}	Xylene	109
947	128	C_9H_{20}	Dimethyl heptane	58
953	110	C_8H_{14}	Bicyclooctane	12
	112	C_8H_{16}	C_8 alkane isomer	12
955	128	$C_8H_{16}O$	Octanone	7
959	128	C_9H_{20}	Methyl octane	109
969	104	C_8H_8	Stryene	11
971	112	C_8H_{16}	Methyl heptene	159
	132	$C_6H_{12}O_3$	2 ethoxy ethyl acetate	
976	126	C_9H_{18}	Trimethyl cyclohexane	5
978	106	C_8H_{10}	Xylene	139
989	126	C_9H_{18}	Methyl ethyl cyclohexane	43
998	124	C_9H_{16}	Bicyclononane	4
1004	128	C_9H_{20}	Trimethyl hexane	185
1013	140	$C_9H_{16}O$	Nonenone	7
1016	124	$C_8H_{12}O$	Ethynyl cyclohexanol	3
1022	126	C_9H_{18}	Trimethyl hexene	48
1031	120	C_9H_{12}	Cumene	17
1035	142	$C_{10}H_{22}$	C_{10} Alkane isomer	50
1042	124	C_9H_{16}	Methyl bicyclooctane	30
1047	142	$C_{10}H_{22}$	Dimethyl octane	38
1053	124	C_9H_{16}	Bicyclononane	8
1057	126	C_9H_{18}	Propyl cyclohexane	141
1061	142	$C_{10}H_{22}$	Dimethyl octane	359
1065	136	$C_{10}H_{16}$	Carene	2

TABLE 4. VOLATILE ORGANIC COMPONENTS IDENTIFIED IN BREATH SAMPLE FROM SAILOR ON BOARD USS GATO [SAMPLE FILE SUEA04.DAT] (continued)

Spec No.	MW	Formula	Identification	Relative Peak Area ($x10^4$)
1070	142	$C_{10}H_{22}$	Methyl nonane	10
1074	140	$C_{10}H_{20}$	Propyl heptene	99
1076	138	$C_{10}H_{18}$	Menthene	4
1077	120	C_8H_8O	Phenyl acetaldehyde	27
1085	124	C_9H_{16}	Spirononane	2
1088	120	C_9H_{12}	Isopropyl benzene	95
1093	142	$C_{10}H_{22}$	C_{10} Alkane isomer	56
1095	140	$C_{10}H_{20}$	Tetramethyl cyclohexane	6
1099	120	C_9H_{12}	Trimethyl benzene	169
1101	142	$C_{10}H_{22}$	C_{10} Alkane isomer	72
1105			Alkane isomer (tent C_{10})	206
1115	142	$C_{10}H_{22}$	Methyl nonane	64
1116	120 156	C_9H_{12} $C_{11}H_{24}$	Methyl ethyl benzene C_{11} alkane isomer	67
1124	140	$C_{10}H_{20}$	Methyl isopropyl cyclohexane	12
1126	154	$C_{11}H_{24}$	C_{11} Alkane isomer	19
1133	118	C_9H_{10}	Methyl styrene	5
1138	120	C_9H_{12}	Trimethyl benzene	81
1139	140	$C_{10}H_{20}$	Methyl isopropyl cyclohexane	40
1144	140	$C_{10}H_{20}$	Butyl cyclohexane	27
1156	142	$C_{10}H_{22}$	n decane	480
1157	142 146	$C_{10}H_{22}$ $C_6H_4Cl_2$	n decane Dichlorobenzene	74
1165	140	$C_{10}H_{20}$	Ethyl octene	53
1175	156	$C_{11}H_{24}$	C_{11} Alkane isomer	27
1179	156	$C_{11}H_{24}$	Methyl decane	61
1180	120 156	C_9H_{12} $C_{11}H_{24}$	Ethyl toluene C_{11} Alkane isomer	56
1183	140	$C_9H_{16}O$	Cyclooctane aldehyde	3
1186	156	$C_{11}H_{24}$	Dimethyl nonane	20
1191	156	$C_{10}H_{20}O$	Vinyl 2 ethylhexyl ether	208
1198	156	$C_{11}H_{24}$	Methyl decane	51

TABLE 4. VOLATILE ORGANIC COMPONENTS IDENTIFIED IN BREATH SAMPLE FROM SAILOR ON BOARD USS GATO [SAMPLE FILE SUEA04.DAT] (continued)

Spec No.	MW	Formula	Identification	Relative Peak Area ($x10^4$)
1202	140	$C_{10}H_{20}$	Cyclodecane isomer	7
1203	152	$C_{10}H_{16}O$	Camphor	3
1208			Alkane isomer	76
1210	140	$C_{10}H_{20}$	Butylcyclohexane	51
1220	120 156	C_9H_{12} $C_{11}H_{24}$	Alkyl benzene isomer C_{11} Alkane isomer	82
1227	138	$C_9H_{14}O$	Trimethyl cyclohexenone (tent)	19
1229	134	$C_{10}H_{14}$	Dimethyl ethyl benzene	13
1238	156	$C_{11}H_{24}$	Dimethyl nonane	149
1243	156	$C_{11}H_{24}$	Methyl decane	63
1244	134	$C_{10}H_{14}$	Propyl toluene	7
1250	138	$C_{10}H_{18}$	Bicyclodecane	10
1256	156	$C_{11}H_{24}$	C_{11} Alkane isomer	110
1259	134	$C_{10}H_{14}$	C_4 Alkyl benzene	8
1267	134	$C_{10}H_{14}$	Ethyl xylene	12
1273			Alkane isomer	71
1281	168	$C_{11}H_{20}O$	Dibutyl allene oxide (tent)	16
1282	154	$C_{11}H_{22}$	Butyl cycloheptane	24
1294	156	$C_{11}H_{24}$	C_{11} Alkane isomer	360
1303	154	$C_{10}H_{18}O$	C_{10} ketone	23
1318	134	$C_{10}H_{14}$	Tetramethyl benzene	13
1319	170	$C_{12}H_{26}$	C_{12} Alkane isomer	84
1327			Alkane isomer	37
1329			Alkane isomer	39
1333			Alkane isomer (tent C_{11})	168
1334	142	$C_{10}H_{22}$	Dimethyl octane	51
1337	122	$C_7H_6O_2$	Benzoic acid	51
1341			Alkane isomer	12
1345	132	$C_{10}H_{12}$	Methyl dihydroindene	3
1350	154	$C_9H_{14}O_2$	Cyclohexyl acrylate	35
1353			Alkane isomer (tent C_{10})	24
1354	168	$C_{12}H_{24}$	Cyclodecane isomer	9

TABLE 4. VOLATILE ORGANIC COMPONENTS IDENTIFIED IN BREATH SAMPLE FROM SAILOR ON BOARD USS GATO [SAMPLE FILE SUEA04.DAT] (continued)

Spec No.	MW	Formula	Identification	Relative Peak Area ($x10^4$)
1358	132	$C_{10}H_{12}$	Ethyl styrene	7
1362	134	$C_{10}H_{14}$	Tetramethyl benzene	5
1367			Alkane isomer (tent C_{11})	122
1372			Cycloalkane isomer (tent C_{12})	40
1374	132	$C_{10}H_{12}$	Tetrahydronaphthalene	4
1378	170	$C_{12}H_{26}$	Dodecane isomer	101
1387	170	$C_{12}H_{26}$	C_{12} Alkane isomer	34
1391			Alkane isomer	34
1402	128	$C_{10}H_8$	Naphthalene	9
1407	138	$C_{10}H_{18}$	Cyclopentylcyclopentane	10
1409	146	$C_{11}H_{14}$	Dimethyl indan	6
1411			Alkane isomer	15
1421	170	$C_{12}H_{26}$	Dodecane isomer	129
1440	184	$C_{13}H_{28}$	Tridecane isomer	93
1450			Alkane isomer	13
1479			Cycloalkane isomer	17
1485	170	$C_{12}H_{26}$	Alkane isomer	15
1496	147	$C_{10}H_{13}N$	Methyl tetrahydroisoquinoline	1
1498			Alkane isomer	21
1503	146	$C_{11}H_{14}$	Methyl tetrahydronaphthalene	2
1510	162	$C_{12}H_{18}$	Dimethyl isobutyl benzene	1
1511	198	$C_{14}H_{30}$	C_{14} Alkane isomer	58
1525	146	$C_{11}H_{14}$	Dimethyl indan	0.5
1539	184	$C_{13}H_{28}$	Tridecane isomer	68
1557	142	$C_{11}H_{10}$	Methyl naphthalene	4
1561			Alkane isomer	15
1568	160	$C_{12}H_{16}$	Isopropyl methyl styrene	2
1612			Alkane isomer	11
1628	154	$C_{12}H_{10}$	Phenyl benzene	2
1630			Alkane isomer	28
1652	168	$C_{13}H_{12}$	Methyl phenyl	0.5

TABLE . VOLATILE ORGANIC COMPONENTS IDENTIFIED IN BREATH SAMPLE FROM SAILOR ON BOARD USS GATO [SAMPLE FILE SUEA04.DAT] (continued)

Spec No.	MW	Formula	Identification	Relative Peak Area ($x10^4$)
1653	198	$C_{14}H_{30}$	Tetradecane isomer	62
1670	156	$C_{12}H_{12}$	Dimethyl naphthalene	2
1688	156	$C_{12}H_{12}$	Dimethyl naphthalene	2
1694	156	$C_{12}H_{12}$	Dimethyl naphthalene	2
1738			Alkane isomer	21
1786			Alkane isomer	20

Table 5: Comparison with Concentrations of VOC's in Tight Buildings, (ppb).

VOC	USS Gato	Tight Building
Formaldehyde	-----	5-40
Toluene	16	10-30
o,m,p-Xylene	25	10-20
Ethylbenzene	4	5-15
Hexane	15	10-25
1,1,1-Trichloroethane	13	50-150
1,1,2,2-Perchloroethylene	-----	40-80
C_7-C_{11} **Alkanes**	348	10-50

[Data from tight buildings were obtained from reference 3. Bold type identifies compounds present in both environments.]

Table 6: Peak Concentrations of VOC's in the USS Gato and the Space Shuttle Cabin (ppb).

USS Gato		Space Shuttle Cabin	
Benzene	> 80		
n Decane	55	Methane	4,420-135,540
C_{11} Alkane isomer	36	**Toluene**	11-7,490
Dimethyl octane	36	1,1,2-Trichloro-1,2,2-trifluoroethane	9-1,330
C_{10} Alkane isomer	29	Ethanal	60-1,260
2-Methyl butadiene	25	Bromotrifluromethane	380-1,190
Dodecane isomer	23	Ethanol	51-960
Dimethyl hexane	20	Butene	683
C_{10} Alkane isomer	**21**	**2-Methyl-2-propanol**	**2-430**
Vinyl-2-ethylhexyl ether	21	2-Methyl pentane	410
n Octane	20	Methanol	8-360
Trimethyl hexane	19	2-Propanone	12-340
Trimethyl benzene	17	**n Hexane**	11-210
Toluene	16	1,3-Dimethyl benzene	1-200
Methyl heptene	16	**C_8 Aliphatic hydrocarbons**	140
[illegible]thyl nonane	15	**C_9 Aliphatic hydrocarbons**	270
Hexane	15	---	---
(Column Total)	(> 464)		(6,468-150,813)

[Data for the space shuttle cabin were adapted from reference 11. Bold type identifies compounds present in both environments.]

Table 7: Cross-match with VOC's Previously Quantified Aboard Submarines.

(1.)	(2.)
Benzene	>80
Ethanol	2
Ethylbenzene	4
m,p-Ethyltoluene	6
Iso-propylbenzene	10
Toluene	1
Trichloroethylene	0.2
Vinylidene chloride	0.3
m,p-Xylene	11
o-Xylene	14
total hydrocarbons	---

[Column 1. lists the compounds from Table 3-2, reference 7, which cross-matched with VOC's listed in table 3. Column 2. lists the concentrations measured aboard USS Gato in ppb.]

atoms per molecule (330 ppb); 3 were monocyclic, aromatic hydrocarbons (> 113 ppb); and 1 was an ether (21 ppb).

Ten compounds (solvents and paints) could be cross-matched with substances previously quantified in submarine atmospheres. None of these exceeded concentrations of 14 ppb (table 7). Very few compounds crossmatched with organic vapors identified in the space shuttle cabin (table 6). The space cabin contained concentrations of contaminants at least 1 order of magnitude higher than in the moored submarine. The total concentration of C_7-C_{11} alkanes in the submarine, 348 ppb, was lower than the total concentration of C_8-C_9 aliphatic hydrocarbons in the space cabin (tables 5,6). The space cabin contaminants were lower in molecular weight than the submarine contaminants.

One of the collector blanks (figure 1) was exposed to internal standards (perfluorobenzene, 3 ppb, and perfluorotoluene, 3 ppb). Notice that the chromatogram of the collector blank was much less complex than that of the expired breath samples. The peaks of the internal standards did not exceed 500,000 counts, while the background counts almost always fell below 20,000 counts. The background counts never exceeded 60,000 as the spectrum scan number varied from 0 to 1,800.

DISCUSSION

AIR QUALITY. The samples of expired breath contained VOC's derived from endogenous metabolites, tobacco smoke, and atmospheric contaminants. Although the investigators did not witness the collections of expired breath, it is reasonable to presume that the subjects avoided smoking while performing the maneuvers of sample collection. If some subjects smoked at the time of sample collection, they could not have provided samples with comparable reconstructed ion chromatograms. In comparing the upper and lower panels of figure 2, the smoker-patient provided a sample of VOC's which was much less complex than provided by the smoker-crewmember. Even if the middle and lower panels of figure 2 were superimposed, they would collectively contain lower concentrations of fewer VOC's than in the crewmember's expired breath.

The reconstructed ion chromatograms were reviewed by Dr. Jeff Wyatt of the Naval Research Laboratory, who observed a resemblance to GC-chromatograms from submarine atmospheres containing high concentrations of C_{10} hydrocarbons. The consultant expressed concern that apparent overloading of the GC column by benzene may indicate an unusual source of benzene in the submarine. Subsequent computer analysis showed benzene to be at a concentration exceeding 80 ppb, which may have been present in the lung as a residual product of cigarette smoking. Later discussions with the Electric Boat Company's atmosphere-control engineers suggested that high concentrations of C_{10} hydrocarbons were likely to evolve from machinery lubricants.

Crossmatching data from the USS Gato with previous analyses of submarine atmospheres showed the presence of fuels, solvents, and paints in very low concentrations (table 7). None of the VOC's exceeded the 90-day limits of exposure in nuclear submarines (7). Nor did the total concentration of VOC's (ca. 3 mg/m^3) exceed the 90-day limit for total hydrocarbons (70 mg/m^3). Trace quantities of monoethanolamines would be expected during patrol as a by-product of scrubbing carbon dioxide. In port, shut-down of the CO_2 scrubber would explain the apparent absence of monoethanolamines from the submarine atmosphere.

While samples of indoor air typically contain 100-150 organic compounds, the samples from USS Gato contained a more complex mixture with higher concentrations of substances. A comparison of the submarine's atmosphere with that in "tight buildings" (table 5) indicated a 7-fold greater concentration of C_7-C_{11} alkanes in the submarine. The spectrum of VOC's in the moored submarine was remarkably different from that in the space shuttle cabin (11). Fewer organic contaminants (n = 152) were identified in the shuttle cabin than in the submarine (n = 466). Until there are measurements of total hydrocarbons, we can only speculate that the quantity of VOC's in the moored submarine is higher than in tight buildings and lower than in space vehicles.

Biological effects have not been observed from exposure to aliphatic and alicyclic hydrocarbons in concentrations below 500 ppm. Aldehydes are strong irritants of the skin, airways, and skin. The threshold for irritation may be as low as 0.01 ppm. Aromatic hydrocarbons are known to be biologically active in concentrations above 25 ppm and there is concern for possible mutagenic effects (9). Our measurments indicated that the concentrations of VOC's aboard USS Gato were below threshold levels for biological effects.

CRITIQUE OF THE ASSAY. A distinct advantage of the GC/MS/COMP assay over GC assays is its capability to rapidly quantify a large number of VOC's mixed in low concentrations (ppb). The technical advantages of Tenax GC {R}, high affinity for organic molecules and porosity for water vapor, allow for concentration of the VOC's into a sample suitable for analysis (17,2). Furthermore, VOC's are stable on Tenax GC {R} for 4 weeks when protected from light in sealed containers at $4^{O}C$ (14).

Limitations of gas chromatography/mass spectrometry and sampling procedures preclude the GC/MS/COMP assay from detecting all classes of VOC's in 1 sample. Inorganic compounds are not measured because of the characteristics of the sorbent material and the GC column. Pollutant oxidants (ozone, 2-5 ppm NO_x, and >25 ppb molecular halogens) may react with VOC's (5,14,17). Highly polar VOC's, such as organic acids, may escape collection by passing through the sorbent polymer (17). Highly volatile organics, such as methane and freon, may also escape collection when carried through Tenax GC {R} in large volumes of polluted gas. This volume-related loss of analyte, called "breakthrough", is a procedural problem related to sampling strategy (5,14). The absence of methane, freons, monoethanolamines, and other low molecular weight substances from the gas samples in this study may be explained by "bre kthrough". Furthermore, compounds were excluded from identification because their spectral peaks [illegible] 50,000 counts (figures 1,2). Limitation of the COMP GC/MS technique can be overcome by modifying the sampling strategy or using supplementary assay techniques. One useful adjunct would be concurrent measurement of total hydrocarbons content.

FUTURE APPLICATIONS. Recognition must be given to the possibility of a gradual change in spectrum of atmospheric VOC's with modification of the engineering plants aboard submarines. In the future, this can best be determined by; (a.) crossmatching current data with a complete data-base of VOC's previously measured in submarines, and (b.) conducting periodic assays of the expired breath in crewmembers.

The sensitivity of the GC/MS/COMP will permit estimation of the body burden by measurement of VOC's in the expired breath. This information will be useful in evaluating the 90-day limits of exposure to atmospheric hydrocarbons. Of additional interest is the possible application of GC/MS/COMP to evaluating the effects of snorkeling on the submarine atmosphere and crewmembers. It is important to know whether snorkeling pollutes or purifies the submarine atmosphere.

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APPENDIX

PROTOCOL FOR TRIAL MEASUREMENTS OF ATMOSPHERIC HYDROCARBONS ABOARD USS BILLFISH, 5 APRIL 1984.

TIME	TEST
2000	Board ship at moor.
2015	Set up for particulate samples, ambient air samples, and duplicate samples.
2030	Begin 8-hr particulate samples at sites A-D. A engine room B torpedo room C control, or crew's berthing D galley, or crew's mess
2100	Thirty-minute collections of ambient air samples at sites A-C. (desire shut down of the ventilation in order to improve chances for identifying contaminants originating from the ship's interior.) Thirty-minute collections of duplicate samples at sites A and D.
2300	Set up the expired breath samples apparatus at sites A and D.
0100	Collect expired breath from 2 crewmembers on site near site D. Collect ambient air samples at site D.
0200	Dismantle the expired breath samples apparatus.
0500	During cooking of breakfast, collect ambient air samples and duplicate samples at site D.
0600	Stop particulate samples at sites A-D.
0630	Depart ship.

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The success of the submarine atmosphere control program has depended solely upon periodic identification of contaminants in the ship's atmosphere. Substances found to exceed safeguard concentrations are controlled by restricting their use aboard ship or scrubbing them from the atmosphere. But, this approach tends to ignore the human host. Advancements in technology now enable biomedical scientists to identify organic gases absorbed by the human body during exposures to industrial environments. We evaluated the potential application of computer-

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assisted gas chromatography mass spectrometry (GC/MS/COMP) to measuring of volatile organic compounds (VOC's) absorbed by submarine crewmembers. Expired breath samples were collected from watchstanders stationed in the forward space, torpedo room, forward engine space, and engineering space of a fast-attack submarine. Analysis of the samples showed a remarkably complex mixture of VOC's with an average of 468 compounds per sample. Without benzene, the total concentration of organic vapors, 3 mg m^3, was well below the maximum allowable concentration of total hydrocarbons (70 mg m^3) for 90 continuous days aboard submarines. Benzene overloaded the sample collected and therefore existed in a concentration > 80 ppb. Since all crewmembers were smokers, one possible source of benzene was residual organic vapors in the lung. Thirteen of the 17 highest concentrations of VOC's were acyclic, C_7-C_{11} alkanes. Assuming that most of the expired VOC's were derived from the submarine, the hydrocarbon composition of the atmosphere was more concentrated and complex than in residential dwellings. This indicates that crewmembers absorb atmospheric VOC's during patrol and desorb the contaminants at home. Future work should attempt to: (a) measure desorption of VOC's from the body after patrol, and (b) evaluate the VOC's likely to overload the sample collector during 20-liter collections of the submarine atmosphere. The desorption of trace contaminants from the body will indicate a body burden of organic substances. > Estimations of body burdens can provide the Navy with an additional guideline for prioritizing gaseous contaminants and judging the quality of air in submarine atmospheres. < Selective use of the GC/MS/COMP technique may also prove useful for evaluating operational problems, such as the minimum required frequency of snorkeling.

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